

# Squeezing the magnetism out of $\text{CaFe}_2\text{As}_2$ – a volume and moment “collapsed” superconducting phase

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**Two recently discovered<sup>1,2,3,4</sup> series of high transition temperature (high- $T_C$ ) superconductors originate from the parent systems  $R\text{FeAsO}$  ( $R$  = rare earth) and  $A\text{Fe}_2\text{As}_2$  ( $A$  = alkaline earth metal), which are tetragonal at room temperature but undergo an orthorhombic distortion in the range 100-220 K that is associated with the onset of antiferromagnetic order<sup>5,6,7,8,9,10,11</sup>. Tuning the system via element substitution<sup>2,3,4,12,13,14</sup> or oxygen deficiency<sup>15,16</sup> suppresses the magnetic order and structural distortion in favour of superconductivity ( $T_C$ 's up to 55 K), with an overall behaviour strikingly similar to the high- $T_C$  copper oxide family of superconductors. However, the recent report of pressure-induced superconductivity in the parent  $A\text{Fe}_2\text{As}_2$ <sup>17,18</sup> opens an alternative path to superconductivity. Here we report that  $\text{CaFe}_2\text{As}_2$  undergoes a pressure-induced**

**transition to a non-magnetic, volume “collapsed” tetragonal phase, which becomes superconducting at lower temperature. Spin-polarized total energy calculations on the collapsed structure find that the magnetic Fe moment itself collapses, consistent with the absence of magnetic order in neutron diffraction and the loss of spin-disorder scattering in resistivity measurements<sup>17</sup>. The loss of the Fe moment raises new questions concerning the role of spin fluctuations as a pairing mechanism for pressure-induced superconductivity in  $\text{CaFe}_2\text{As}_2$ , as proposed for the doped iron arsenids<sup>5</sup>.**

Recent investigations of the superconducting iron-arsenide families have highlighted the role of pressure, be it chemical or mechanical, in fostering superconductivity. Perhaps most intriguing is the discovery that, under quite modest applied pressure, the distinct resistivity signature of the first-order tetragonal-to-orthorhombic and magnetic phase transition<sup>19</sup> in  $\text{CaFe}_2\text{As}_2$  is suppressed<sup>17</sup> and superconductivity emerges at lower temperature for pressures between 0.35 GPa and 0.86 GPa<sup>17</sup>. The pressure-induced superconductivity in  $\text{CaFe}_2\text{As}_2$  was confirmed<sup>20</sup> and followed by observations of superconductivity for  $\text{BaFe}_2\text{As}_2$  and  $\text{SrFe}_2\text{As}_2$  at significantly higher pressures<sup>18</sup>. In this respect the iron arsenides bear a similarity to other exotic superconductors, such as  $\text{CeRhIn}_5$ <sup>21</sup>, where the appearance of superconductivity with pressure is associated with proximity to a quantum critical point. In  $\text{CaFe}_2\text{As}_2$ , a second high-temperature phase transition, associated with the loss of spin-disorder scattering, is observed above 0.55 GPa<sup>17</sup> by anomalies in resistivity. However, the nature of the phase at temperatures below this transition and its relation to the ambient-pressure tetragonal and orthorhombic phases are as yet unknown. Neutron scattering experiments on polycrystalline  $\text{CaFe}_2\text{As}_2$  were performed to enlighten these issues.

Figure 1 shows neutron diffraction scans taken through the nuclear  $(0\ 0\ 2)$ ,  $(2\ 2\ 0)_T$ , and magnetic  $(1\ 2\ 1)_{OR, magnetic}$  diffraction peaks at selected temperatures and pressures. At 50 K and ambient pressure (A), the splitting of the  $(2\ 2\ 0)_T$  into the orthorhombic  $(4\ 0\ 0)_{OR}/(0\ 4\ 0)_{OR}$  peaks signals the existence of the orthorhombic phase (Fig. 1(b)). This, together with the observation of the  $(1\ 2\ 1)_{OR, magnetic}$  peak (Fig. 1(c)), is consistent with previous x-ray and neutron diffraction measurements at ambient pressure<sup>10,19</sup>. Upon increasing pressure at  $T = 50$  K, the structure remains orthorhombic and antiferromagnetic up to approximately 0.24 GPa. Between 0.24 and 0.35 GPa, dramatic changes take place in the measured diffraction patterns. At pressures above 0.35 GPa (Fig. 1(c)), the magnetic peak is absent and the orthorhombic structure has transformed to a tetragonal phase, similar to the high temperature ambient pressure structure, but with extraordinarily different lattice parameters. This is most evident from the strong shift in position of the  $(0\ 0\ 2)$  peak at (B) in Fig. 1(a). Upon cooling to 4 K, within the superconducting regime<sup>17</sup>, the “collapsed” tetragonal structure remains unchanged.

The central region (shown in yellow) of Figs. 2(b) and (c) shows the results of Rietveld refinements of the lattice parameters and volume for this “collapsed” tetragonal phase. We find an astonishing 9.5% reduction in the  $c$ -lattice parameter with respect to the orthorhombic phase and a nearly 5% decrease in the unit cell volume. Even more striking is the reduction of the  $c/a$  ratio, a key parameter for bond geometries in the iron arsenides, by nearly 11%. As a consequence, the As-Fe-As bond angles change strongly as illustrated in Fig. 2(d).

With the pressure maintained at 0.63 GPa, the temperature was raised in 50 K steps (right panels of Fig. 2). Between 150 and 200 K an isostructural transition between the low-temperature “collapsed” tetragonal phase and the high temperature tetragonal structure is observed. Upon release of the pressure at 250 K, the curves labelled (D) in

Fig. 1 show only small changes in the lattice parameters between 0.63 GPa and ambient pressure, providing a measure of the modest, but strongly anisotropic compressibility of the high temperature phase. We note that there is a difference of about 50 K between the temperature of the isostructural transition at 0.63 GPa measured here and that reported in transport measurements<sup>17</sup>. However, as pointed out in Ref. 17, the resistive anomalies are rather broad in applied pressure, and different criteria for the definition of transition temperatures can shift temperature assignments. In addition, the data in Ref. 17 were taken with decreasing temperature whereas here the temperature was stepwise increased. With these uncertainties understood, the tetragonal-to-“collapsed” tetragonal transition appears to be responsible for the loss of resistivity whose locus defines the high temperature, high-pressure phase line found in Ref. 17 and shown in Fig. 2(a).

In order to relate the volume change to relative changes in the unit cell dimensions, and to verify the stability of this phase, spin-polarized total energy calculations were performed for volume changes of  $\Delta V/V = 0\%$  (for ambient pressure) and  $\Delta V/V = -5\%$  (for the “collapsed” phase). From the blue curves in Fig. 3(a) we see that, for ambient pressure, the orthorhombic magnetic phase is lowest in energy, consistent with our ambient pressure low temperature measurement. The red curves in Fig. 3(a) show that the tetragonal phase is lowest in total energy for the 5% volume reduction. The minimum energy of this “collapsed” tetragonal phase is found at  $c/a \approx 2.65$ , close to the experimental value of 2.67 (Fig. 2(c)). The  $c/a$ -dependence of the spin-polarized total energy calculations for the “collapsed” phase can be correlated with a loss of the Fe magnetic moment, as shown in Fig. 3(b). The astonishing result of a quenched magnetic moment ground state is consistent with our observation of the loss of magnetic order in the “collapsed” tetragonal phase as well as the loss of spin-disorder scattering in resistivity measurements, and further confirmed by the additional non-spin-polarized total

energy calculations (see red stars in Fig. 3(a)). The band structure calculations also indicate that several bands cross the Fermi level at the pressure-induced transition.

The principal result of these neutron diffraction measurements is the discovery of a transition from the magnetically ordered orthorhombic phase to a non-magnetically ordered “collapsed” tetragonal phase preceding the onset of superconductivity. Further, the second, higher pressure, transition noted in transport measurements<sup>17</sup> has been identified as an isostructural transition between the pressure-induced “collapsed” phase and the high-temperature tetragonal structure. The loss of spin disorder scattering postulated in Ref. 17 follows from the loss of magnetic moment in the “collapsed” tetragonal phase. We note that the observed volume reduction can also serve to increase the charge carrier density. The schematic phase diagram in Fig. 3(c) summarizes our findings. The structure of the pressure-induced “collapsed” phase is unchanged in the superconducting state determined by measurements at 4 K and under 0.48 GPa. It seems clear then, that the pressure-induced superconductivity in  $\text{CaFe}_2\text{As}_2$  emerges from the “collapsed” tetragonal phase rather than the magnetically ordered, orthorhombic phase or the higher temperature, ambient pressure, tetragonal phase.

Anomalous changes in the unit cell volume and lattice constants have also been noted in the  $R\text{FeAsO}$  system. In superconducting fluorine-free oxygen-deficient samples of  $\text{NdFeAsO}_{1-\delta}$ , a surprising discontinuous decrease in the lattice parameters and unit cell volume ( $\Delta V/V = -1.8\%$ ) was found for  $\delta = 0.4$ , where a maximum in the superconducting volume fraction is observed<sup>16</sup>. Furthermore, a correlation between superconducting transition temperatures for  $R\text{FeAsO}_{1-\delta}$  and the unit cell dimensions is reported in Ref. 15. In light of our results, it appears that chemical substitution and the introduction of oxygen deficiency likely play a dual role in the iron arsenide superconductors by increasing the

charge carrier density *and* changing the “chemical pressure”. It is not yet clear which has the greater impact upon superconductivity.

Given that the RFeAsO and AFe<sub>2</sub>As<sub>2</sub> families share a common structural element (FeAs layers) and similar prerequisites for superconductivity (e.g. suppression of magnetic order) it is useful to elucidate structural quantities that are shared and can be correlated with superconducting properties. In Figure 3(d) we plot the measured superconducting transition temperatures  $T_C$ , for those iron-arsenide compounds that are superconducting, as a function of the variance  $\sigma^2$  of the As-Fe-As bond angles as described in Fig. 2(d). As  $\sigma^2$  increases, corresponding to greater deviations in the bond angle from the ideal tetrahedral angle,  $T_C$  decreases. The pressure-dependent properties of the “collapsed” tetragonal phase of CaFe<sub>2</sub>As<sub>2</sub> described above clearly continue this trend and allow generalizing our result to the family of Fe-As based superconductors. The high value for  $\sigma^2$  in the “collapsed” tetragonal phase for CaFe<sub>2</sub>As<sub>2</sub> is consistent with the low  $T_C$  in comparison to other Fe-As based superconductors. The observed correlation between  $T_C$  and  $\sigma^2$  points to the importance of the structure and the symmetry in the Fe-As network for the superconducting state. Properties that are sensitive to the As-Fe-As bonding geometry and its symmetry, such as anisotropic magnetic or elastic couplings in the Fe-As network, seem strongly involved in the superconducting pairing.

These results highlight intriguing questions that point to the potential complexity of the superconducting state in the iron arsenides. From the analysis of  $T_C$  as a function of the As-Fe-As bond angle variance, we have found that superconductivity in the “collapsed” tetragonal phase fits well within the general trend observed for the doped iron arsenides, implying a common superconducting pairing mechanism. It has been suggested that spin-fluctuations are responsible for the electron pairing in this class of superconductors<sup>5</sup>. The loss of a static moment in the “collapsed” tetragonal phase may

seem inconsistent with such a magnetic pairing mechanism for the pressure-induced superconductivity in  $\text{CaFe}_2\text{As}_2$ . However, the strong pair-breaking effect of local moments is eliminated and superconductivity mediated by paramagnons<sup>22</sup> remains a possibility.

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**Supplementary Information**, e. g. details of neutron diffraction measurements and their analysis including structure data, and details of the spin-polarized total energy calculations, accompanies the paper on [www.nature.com/nature](http://www.nature.com/nature).

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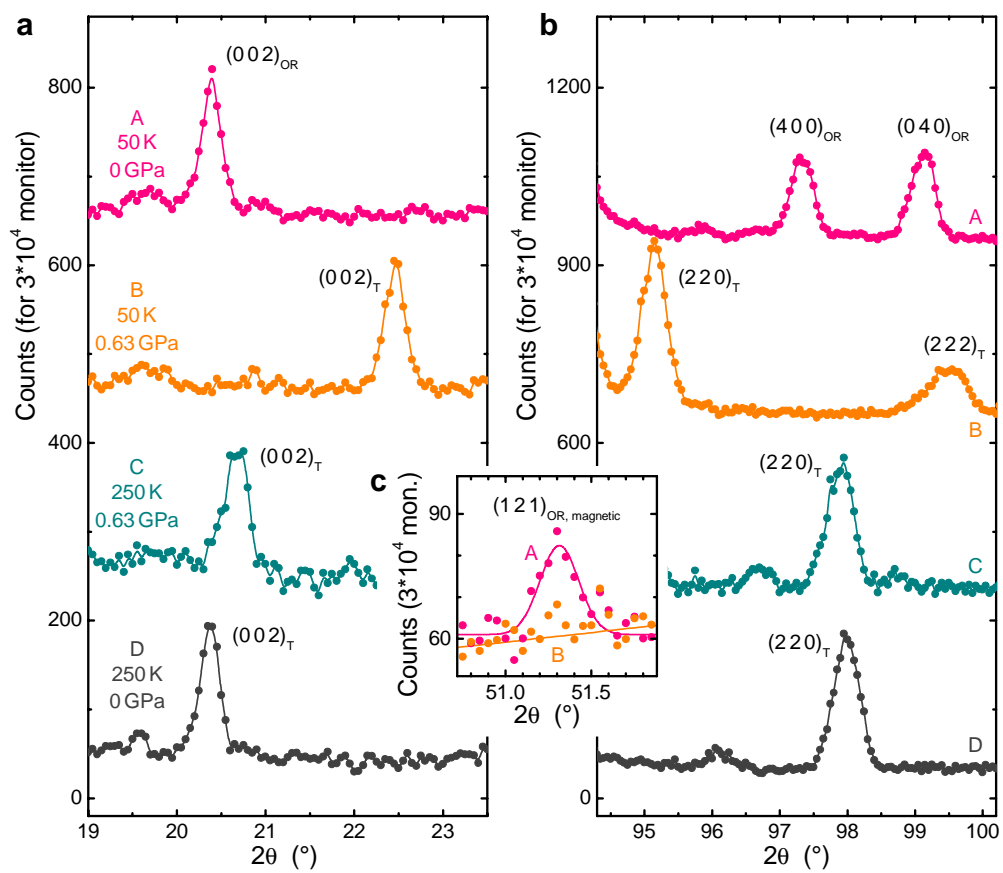
**Figure 1. Scans through nuclear and magnetic peaks in neutron diffraction pattern at selected temperatures and pressures. a-c,** Special attention was paid to maintain experimental conditions closest to the reported macroscopic measurements and under well-defined hydrostatic pressure. Therefore, the experiments were performed on a polycrystalline sample prepared out of approximately 1.75 grams of single crystalline  $\text{CaFe}_2\text{As}_2$  material grown using the procedure described in references 19, and 23. Temperature-dependent resistance measurements on these crystals reproduced the data presented in references 17 and 19. The sample was loaded into a He-gas pressure cell (maximum pressure 0.63 GPa) and measured on the high resolution powder diffractometer BT1 at the NIST Center for Neutron Research. For the temperature dependent studies, the temperature was slowly changed with a maximum rate of 5 K/min while the pressure was adjusted and allowed to equilibrate between measurements. To reduce the effects of preferred orientation, the sample was oscillated over an angle of  $36^\circ$  during each measurement. The selected pressures and temperatures are denoted as points A, B, C, and D in Figure 2(a) in the  $p$ - $T$  phase diagram with respect to phase lines determined by transport measurements<sup>17</sup>. Note that the diffraction peaks change position dramatically due to the huge change in lattice parameters. In (c), the magnetic  $(121)_{\text{OR, magnetic}}$  diffraction peak for point A is clearly observed above the background taken at B. No new magnetic peaks for B and C were observed. Unlabelled peaks in the pattern arise from phases other than  $\text{CaFe}_2\text{As}_2$ , such as minor contamination from the Sn flux or  $\text{SiO}_2$ , or the pressure cell. The subscripts denote the crystal structure used for indexing (T = tetragonal; OR = orthorhombic). The offset between every data set is 200 Counts/ $3 \times 10^4$  monitor in (a) and 300 Counts/ $3 \times 10^4$  monitor in (b), respectively.

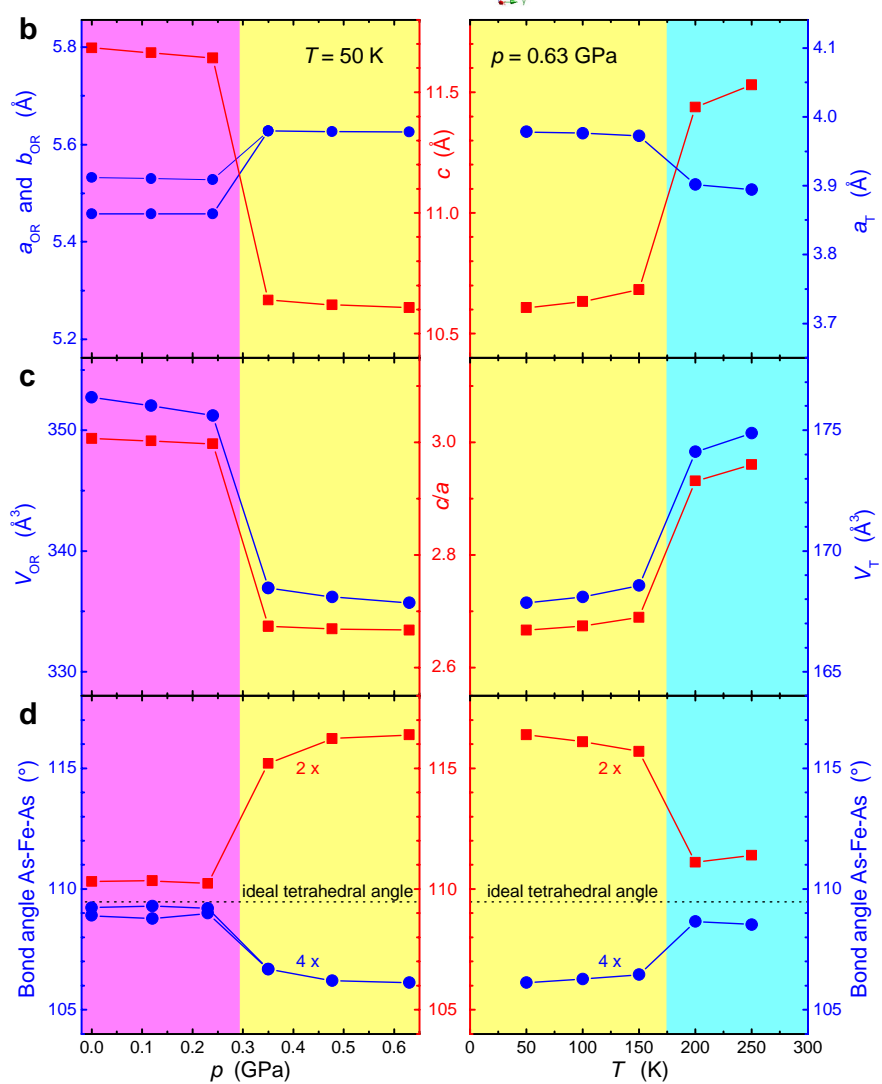
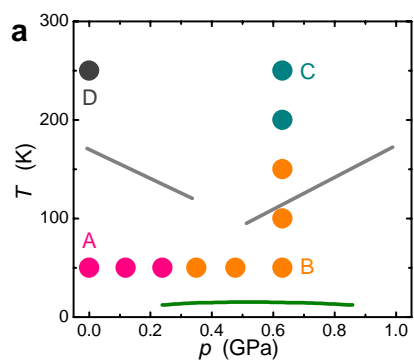
**Figure 2. Schematic phase diagram and pressure and temperature dependence of the lattice parameters, unit cell volume and As-Fe-As bond angles.**

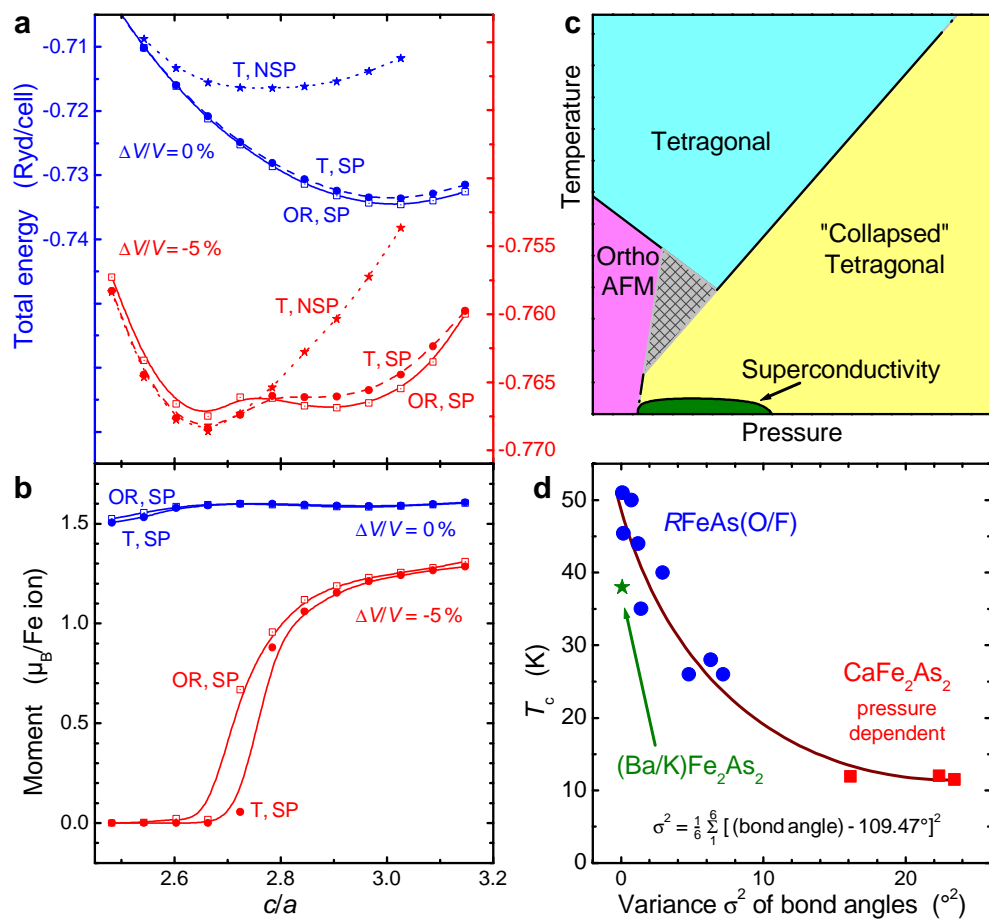
**a, (left panel)** Lines in the schematic  $p$ - $T$  diagram denote the high pressure phase lines determined in reference 17. Points A – D label the pressures and temperatures for the diffraction data shown in Figure 1. Once loaded into the pressure cell, the sample temperature was lowered to 50 K and diffraction patterns were obtained as the hydrostatic pressure was increased to a maximum of 0.63 GPa. At this pressure, the temperature was then increased in 50 K steps to 250 K. **a, (right panel)** The unit cell of the tetragonal phase of  $\text{CaFe}_2\text{As}_2$ . **b,-d,** Pressure dependence **(left panels)** at  $T = 50$  K and temperature dependence **(right panels)** at  $p = 0.63$  GPa **b,** of the lattice parameters, **c,** of the unit cell volume and  $c/a$  ratio, and **d,** of the As-Fe-As bond angle. The structure data (lattice parameters and atomic-position parameter  $z_{\text{As}}$  of As) were determined by Rietveld refinements using the GSAS software package<sup>24</sup>. Of particular interest is the comparison of the As-Fe-As bond angles with the ideal tetrahedral value of  $109.47^\circ$ . For this special value all Fe atoms are coordinated in ideally formed tetrahedrons with identical high-symmetric Fe-As-Fe-bonding geometries [highlighted in brown in the right panel of (a)]. This symmetry is broken for As-Fe-As bond angles deviating from this ideal angle yielding two or three different values in the tetragonal or orthorhombic structure, respectively. The variance in deviation of the Fe-As-Fe-bonding angles from the ideal value parameterizes the strength of this symmetry breaking and is used to correlate superconducting properties to this structural parameter in Fig. 3(d).

**Figure 3. Summary of the results of the neutron diffraction measurements**

**and total energy calculations. a,** Spin-polarized (SP) and non-spin-polarized (NSP) total energy calculations for  $\Delta V/V = 0\%$  and  $\Delta V/V = -5\%$  for the tetragonal (T) and orthorhombic (OR) phases (Note the different energy scales). For the spin-polarized and non-spin-polarized calculations, the local density approximation was employed, using the full potential linearized augmented plane wave method with the Perdew-Wang 1992 functional<sup>25</sup>. The precision of the total energy is 0.01 mRyd/cell, much smaller than the size of the symbols. For ambient pressure, the orthorhombic magnetic phase is lowest in total energy, while for the compressed volume the “collapsed” tetragonal phase is lowest in total energy. Both the spin-polarized and non-spin-polarized calculations yield the same total energy minimum for the non-magnetic “collapsed” tetragonal phase at the same  $c/a$  ratio (in tetragonal notation). **b,** For the “collapsed” phase, the Fe moment is quenched at the minimum in total energy in the spin-polarized calculation. **c,** Schematic  $p$ - $T$  diagram based upon the diffraction and transport<sup>17</sup> measurements. Dashed lines represent estimates of the phase boundaries. The cross hatched area indicates a region where precise details of how these transition lines intersect still needs to be determined. **d,** Correlation between the superconducting transition temperatures and the variance of the As-Fe-As bond angle (defined as the root mean square difference between the measured bond angles and the ideal tetrahedral value of  $109.47^\circ$ ). The data were obtained from Refs. 5 and 26-30 for the  $R\text{FeAs}(\text{O/F})$  compounds and from Ref. 4 for  $(\text{Ba/K})\text{Fe}_2\text{As}_2$ , respectively. The data for  $\text{CaFe}_2\text{As}_2$  are derived from the present measurements.









Supplementary Information A for A. Kreyssig *et al.*

### **Details of the neutron diffraction measurements and their analysis including structure data**

The neutron diffraction measurements were performed on the high resolution powder diffractometer BT1 at the NIST Center for Neutron Research using a wavelength of 2.0782 Å selected by a Ge (3 1 1) monochromator. The collimation of the incident beam was set at 15'.

Special attention was paid to maintaining experimental conditions closest to the reported macroscopic measurements and to perform the study under well-defined hydrostatic pressure. The soft and ductile nature of the compound presents challenges for powder diffraction measurements since flux-grown single crystals tend to smear and shear when ground into a powder. The effects of grinding are clearly observed as broadened peaks in x-ray powder diffraction measurements, and the modification of physical properties associated with grinding have not yet been characterized. Therefore, as-grown single crystals ( $\approx 500$ -1000) were loaded into an Al-alloy He-gas pressure cell and cooled using a top-loading closed-cycle cryogenic refrigerator. The pressure cell was connected to a pressurizing intensifier through a high pressure capillary. Hydrostatic pressure was maintained throughout the measurements since the temperature was kept well above the melting curve for helium (for pressures up to 0.63 GPa). For the temperature dependence studies, the temperature was slowly changed with a maximum rate of 5 K/min while the pressure was adjusted and allowed to equilibrate between measurements.

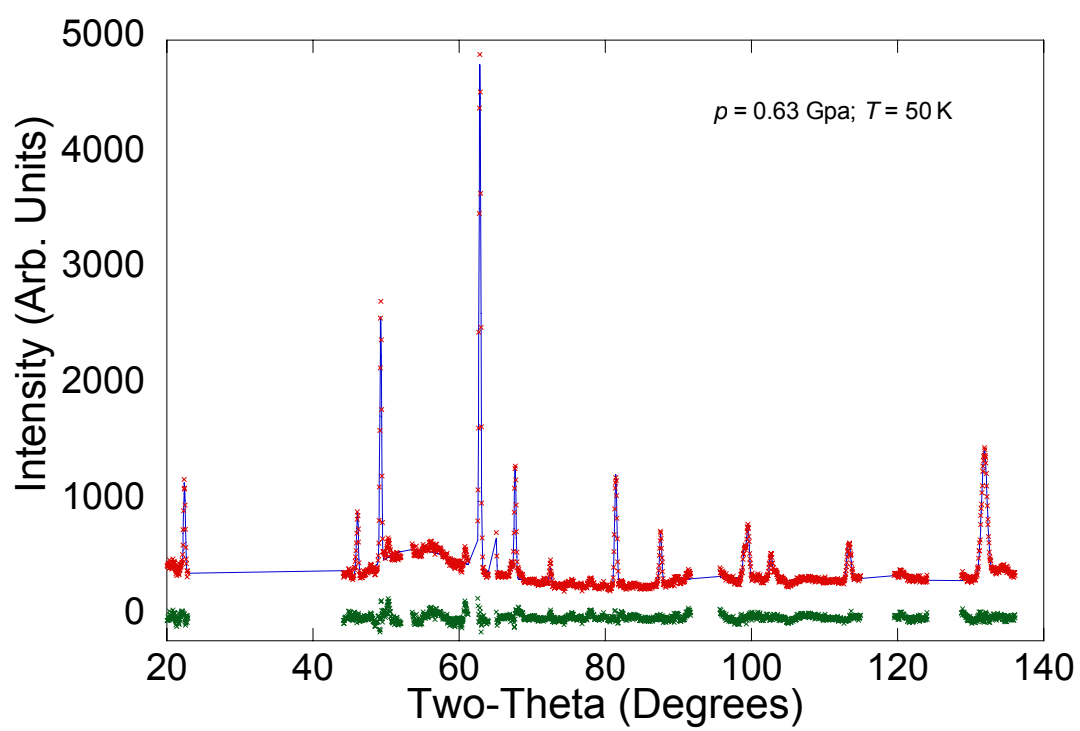
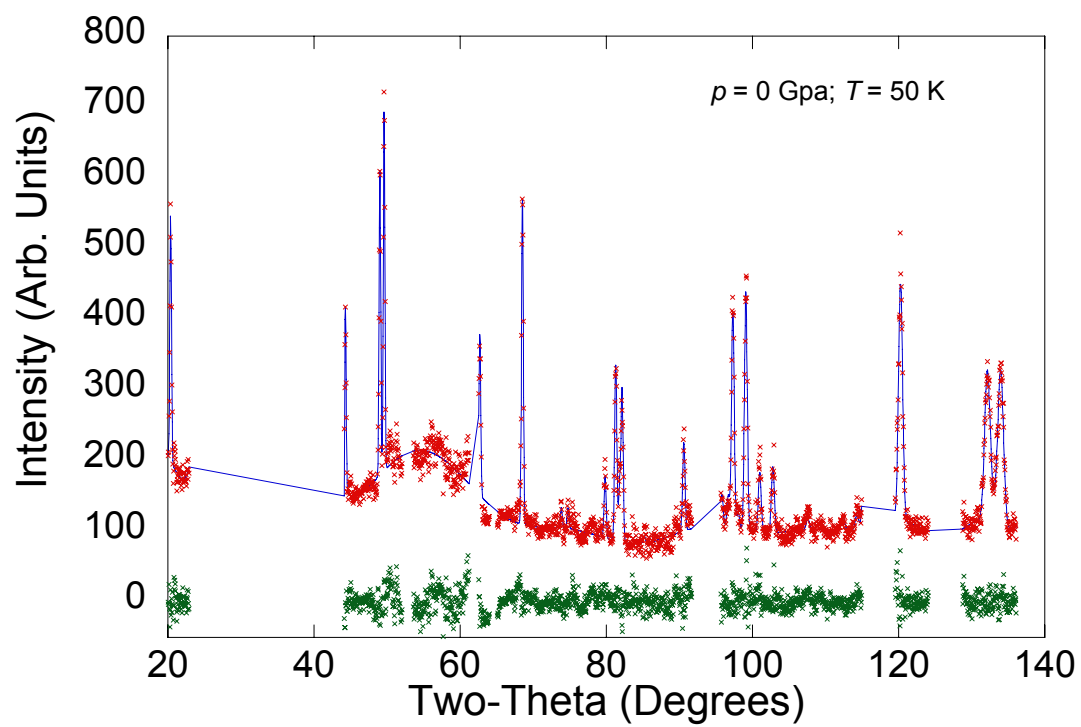
To reduce the effects of preferred orientation, the sample was oscillated over an angle of 36° during each measurement. Nevertheless, a degree of preferred orientation remained but was adequately modelled in subsequent Rietveld refinements using the GSAS software package. For each diffraction pattern approximately 70 reflections were used to refine the lattice parameters, the z coordinate of the As ions and the 12 parameters associated with corrections for preferred orientation. We point out that the correction for preferred orientation remained constant over all pressures and temperatures measured and were taken as constants in the fits. Typical  $R$ -values ( $wR_p$ ), representing the goodness-of-fit, were between 4-5% for all fits demonstrating the accuracy of the model employed.

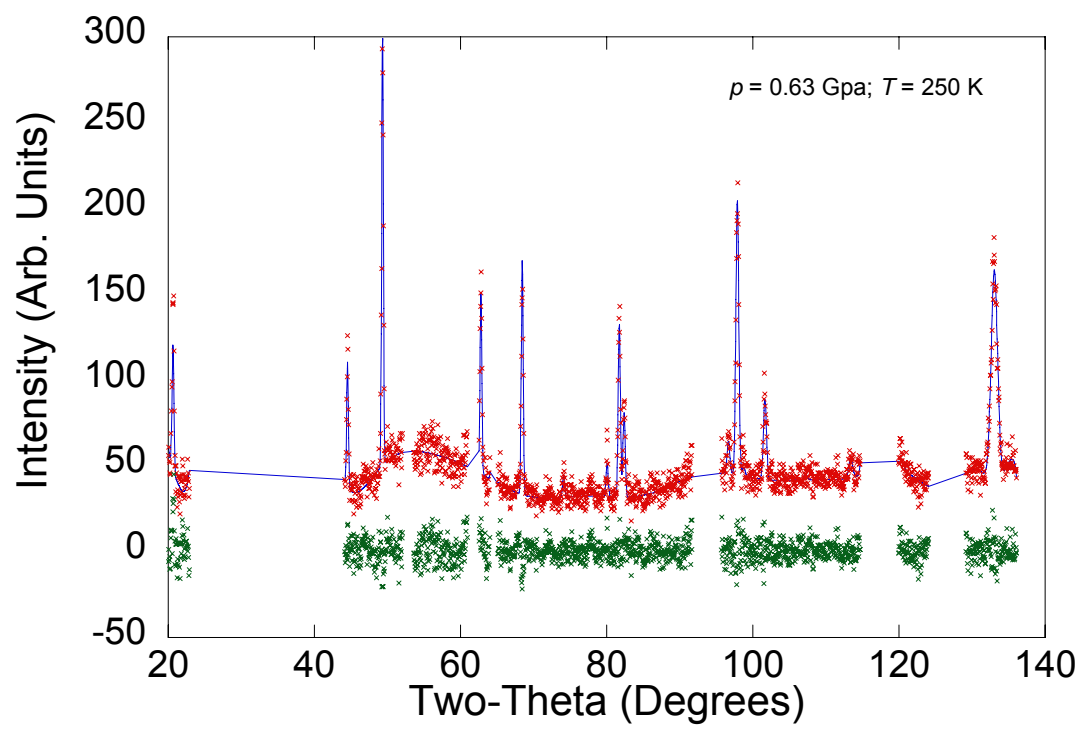
**Results of Rietveld refinements for pressure-dependent measurements at a temperature  $T = 50$  K**

<b>Pressure</b> <b><math>p</math> (GPa)</b>	<b>0</b>	<b>0.115</b>	<b>0.24</b>	<b>0.35</b>	<b>0.47</b>	<b>0.63</b>
<b><math>a</math> (Å)</b>	5.5312(2)	5.5294(2)	5.5275(2)	3.9792(1)	3.9785(1)	3.9780(1)
<b><math>b</math> (Å)</b>	5.4576(2)	5.4577(2)	5.4575(2)			
<b><math>c</math> (Å)</b>	11.683(1)	11.6625(8)	11.6391(9)	10.6379(6)	10.6178(7)	10.6073(7)
<b>Volume <math>V</math> (Å<sup>3</sup>)</b>	352.68(4)	351.94(3)	351.11(3)	168.44(1)	168.07(1)	167.85(1)
<b><math>z_{\text{As}}</math></b>	0.3689(5)	0.3693(4)	0.3690(4)	0.3687(7)	0.3657(7)	0.3663(5)
<b>Fe-As (Å)</b>	2.388(6)	2.3891(3)	2.3854(3)	2.3560(4)	2.343(3)	2.340(3)
<b>Fe-Fe (Å) (2x)</b>	2.7656(1)	2.76469(8)	2.7637(1)			
<b>Fe-Fe (Å) (2x)</b>	2.7288(1)	2.72882(7)	2.72874(8)			
<b>Fe-Fe (Å) (4x)</b>				2.8137(9)	2.8132(1)	2.8128(1)

**Results of Rietveld refinements for temperature-dependent measurements  
at a pressure  $p = 0.63$  GPa**

Temperature $T$ (K)	50	100	150	200	250
$a$ (Å)	3.9780(1)	3.9760(3)	3.9724(2)	3.9015(2)	3.8944(2)
$c$ (Å)	10.6073(7)	10.633(1)	10.683(1)	11.438(2)	11.530(2)
Volume $V$ (Å <sup>3</sup> )	167.85(1)	167.95(3)	168.57(3)	174.11(3)	174.87(3)
$z_{\text{As}}$	0.3663(5)	0.3668(9)	0.3669(9)	0.367(1)	0.3652(8)
Fe-As (Å)	2.340(3)	2.344(5)	2.346 5	2.365(9)	2.357(5)
Fe-Fe (Å) (4x)	2.8128(1)	2.8115(2)	2.8089(2)	2.7588(2)	2.7538(1)





Supplementary Information B for A. Kreyssig *et al.*

### Details of the spin-polarized total energy calculations

For the spin-polarized and non-spin-polarized calculations, the local density approximation was employed, using the full potential linearized augmented plane wave method with the Perdew-Wang 1992 functional. The convergence criterion for the total energy was 0.01 mRyd/cell. The calculations were done in the tetragonal phase (two formula units) for two different cell volumes as the  $c/a$  ratio was varied: 0% volume reduction using the experimentally determined lattice parameters and for a 5% volume reduction. The calculations were also performed for the orthorhombic phase, with  $a/b = 1.02$ , for both 0% and 5% volume reduction. The experimental value of the internal parameter was used for the calculations [1]. The  $R_{\text{MT}} * K_{\text{max}}$  that determines matrix size (the number of the basis functions), where  $R_{\text{MT}}$  is the smallest of all atomic sphere radii and  $K_{\text{max}}$  is the plane wave cut-off was set to 8.0. The muffin-tin radii ( $R_{\text{MT}}$ ) for the 0% volume reduction calculation were 2.2, 2.1 and 2.1 atomic unit for Ca, Fe and As, respectively. For the 5% reduction calculation, the  $R_{\text{MT}}$  also were scaled to keep the matrix size the same. There were 100  $k$ -points used in the irreducible Brillouin zone.

[1] Wu, G. *et al.* Different resistivity response to spin density wave and superconductivity at 20 K in  $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ , arXiv:0806.4279 (2008)